Occurrence of By-Products of Strong Oxidants Reacting with Drinking Water Contaminants—Scope of the Problem

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This paper describes results of a detailed literature review of the organic and inorganic by-products that have been identified as being formed in aqueous solution with four of the strong oxidizing/disinfecting agents commonly employed in drinking water treatment. These agents are: chlorine, chlorine dioxide, chloramine, and ozone.

Significant findings include the production of similar nonchlorinated organic oxidation products from chlorine, chlorine dioxide, and ozone. In addition, all three chlorinous oxidants/disinfectants can produce chlorinated by-products under certain conditions. The presence of chloronitrile compounds in drinking waters is indicated to arise from reactions of chlorine or chloramine to amine/amide functions in amino acids or proteinaceous materials, followed by dehydrohalogenation. These nitriles could hydrolyze to produce the corresponding chloroacetic acids.

It is concluded that to minimize the presence of oxidation by-products in drinking waters, the concentrations of oxidizable organic/inorganic impurities should be lowered before any oxidizing agent is added.

Introduction

This paper is concerned with the by-products of chemical oxidizing agents that are used in the treatment of drinking water (chlorine, chlorine dioxide, ozone, chloramine), sometimes for disinfection, sometimes for chemical oxidation, and sometimes for both purposes. Most of the chemicals currently used as disinfectants also are powerful oxidizing agents, and many times, water treatment processes use these chemical oxidizing agents during pretreatment, rather than during the terminal disinfectant step. For example, potassium permanganate and ozone are used for iron and manganese or taste and odor removal. It is thus important for health effects professionals to recognize that the so-called disinfection by-products will be present following oxidative pretreatment, even though disinfection may not yet have been practiced during the water treatment process.

As a result, the water treatment specialist must understand the chemistries involved in the following topics: the by-products of the chemical oxidizing agents as they are reduced while doing their oxidation/disinfection work during water treatment; reactions of chemical oxidizing agents with organic materials present at the point of addition of oxidant/disinfectant, i.e., by-prod-

ucts of organic materials; and reactions of chemical oxidizing agents with inorganic materials present at the point of addition of oxidant/disinfectant, i.e., by-products of inorganic materials.

Objectives

This paper summarizes the most significant findings of a detailed survey of the literature, funded by the U.S. Environmental Protection Agency (EPA), Office of Drinking Water. The objectives of this program were to survey and analyze the published literature dealing with known oxidation chemistries of products formed when various oxidizing agents are used during drinking water treatment processes. Eight specific oxidizing agents were studied; first priority was given to chlorine, chlorine dioxide, ozone, and chloramine; second priority was given to potassium permanganate, hydrogen peroxide, bromine, and iodine.

The major findings of this study are presented in this paper for the four first-priority compounds. Each of the first-priority oxidants will be discussed in terms of the by-products of the oxidants themselves (e.g., those materials which form from the oxidant as it is reduced), as well as by-products isolated as a consequence of oxidation of the soluble substrates. In the case of halogen oxidants, we will also discuss some of the halogenated materials obtained during treatment of soluble substrates.

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Table 1. Relative oxidation power of various oxidizing species.

Species	Oxidation potential, at 25°C, V[a]	Relative oxidation power[b]
Hydroxyl free radical	2.80	2.05
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Permanganate ion	1.49	1.10
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00
Hypobromous acid	1.33	0.98
Chlorine dioxide	1.275	0.94
Monochloramine	1.16	0.85
Hypoiodous acid	0.99	0.73

[a] Relative to the hydrogen electrode.
[b] Based on chlorine as reference (= 1.00).

Chemistry of Oxidants/Disinfectants

Oxidation is defined as a loss of electrons; reduction as a gain of electrons. During oxidation/reduction reactions, as one component (the soluble substrate = SS) is chemically oxidized, the oxidizing agent is chemically reduced. Halogen-containing oxidants/disinfectants provide an additional complication, however, in that these materials also can undergo halogenation reactions.

It should be recognized, however, that the halogen compounds commonly used in drinking water treatment (particularly chlorine) give rise to both halogenation and oxidation/reduction reactions and that these reactions usually occur simultaneously. Furthermore, it has been estimated that in the case of chlorine added to aqueous solutions containing soluble organic substrates capable of being oxidized/chlorinated, only 10% of the chlorine added results in the production of chlorinated compounds (1,2). Thus 90% of the chlorine added reacts solely as an oxidizing agent, producing nonchlorinated organic oxidation products.

Oxidation Potentials

Some measure of the ability of the various oxidants to oxidize soluble substrates can be gathered from consideration of their relative oxidation potentials, shown in Table 1 for the oxidants included in this project. However, it should be appreciated that each chemical oxidation reaction proceeds at a specific reaction rate, governed by kinetics, and affected by a variety of factors, such as concentrations of substrate/oxidant, temperature, pH, the presence of other materials capable of reacting with the oxidant, and the production of oxidation by-products, many of which also can react with the oxidant.

It must also be realized that even though some oxidizing agents with high oxidation potentials also are excellent disinfecting agents (ozone, chlorine, hypochlorous acid, chlorine dioxide), other strong oxidants are poor disinfectants (permanganate, hydrogen peroxide).

Oxidant Characteristics

Table 2 compares the pertinent attributes of each of the eight oxidants/disinfectants considered in this study

Table 2. Comparison of relative effectiveness of oxidants/ disinfectants.

| Oxidant	Disinfecting efficiency	Oxidizing efficiency	Halogenation capability
Chlorine	High	High	Low
ClO_2 (pure)	High	High	Low
ClO_2 (made from $NaClO_2$ + excess chlorine)	High	High	Variable, depending on amount of free chlorine
$ClNH_2$	Low	Low	Low
Ozone	High	High	Zero (except when bromide is present)
$KMnO_4$	Low	High	Zero
H_2O_2	Low	Moderate	Zero
Bromine	High	Low	High
Iodine	High	Very low	Low

in terms of their relative ability to disinfect, to oxidize, and to halogenate.

# By-Products of Strong Oxidants/ Disinfectants

Pertinent literature reports for each of the four primary oxidants/disinfectants (chlorine, chlorine dioxide, chloramine, and ozone) will be summarized with respect to their reactions with specific types of organic materials that are or can be expected to be encountered in drinking water supplies: by-products of the disinfectant itself, reactions with inorganic substrates, reactions with organic aliphatic substrates, reactions with amino acids, reactions with organic aromatic substrates, reactions with heterocyclic substrates, and reactions with humic and fulvic substrates. However, only the major findings of the literature study are discussed, particularly as they relate to drinking water treatment.

## Specific By-Products of Oxidants/ Disinfectants

Chlorine. As is widely understood by water treatment specialists, chlorine gas reacts with water at a pH value just below 7 to produce hypochlorous acid (HOCl) and chloride ion (Cl$^-$):

$$Cl_2 + H_2O \rightarrow HOCl + Cl^-$$
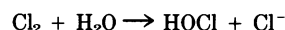
As the pH is raised, hypochlorous acid dissociates to hypochlorite ion (OCl)$^-$. However, this is an equilibrium reaction which is controlled entirely by pH:

$$HOCl + H_2O \rightleftharpoons (OCl)^- + H_3O^+$$
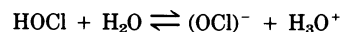
When these species (HOCl, OCl$^-$) oxidize substrates, the chlorine moieties are chemically reduced to chloride ion:

$$HOCl \text{ [or (OCl)}^-] + SS \rightarrow SS_{oxid} + Cl^-$$
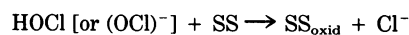
where SS denotes soluble substrate and SS_{oxid} denotes oxidized soluble substrate.

Chloride ion cannot be reoxidized by free chlorine, and, therefore, once formed, it remains as a permanent by-product.

Chlorine Dioxide. Unlike chlorine, pure chlorine dioxide (ClO_2) does not react at significant rates with water or ammonia at neutral pH ranges. However, because chlorine dioxide usually is generated in drinking water treatment plants by reaction of chlorine with chlorite ion, solutions of ClO_2 may contain some amount of free chlorine. Thus the use of chlorine dioxide might be expected to produce some of the same chlorination products as does chlorine, but at much lower concentrations, depending upon how much free chlorine is present after synthesis of ClO_2.

Photolysis experiments by Zika et al. (*3*) showed that ClO_2 decomposes to chlorite ion, ClO_2^-. However, chlorite ion also has a short lifetime in full sunlight (less than 10 min), decomposing to ClO_2 and hypochlorite anion (OCl^-). Therefore, under sunlight conditions, even pure chlorine dioxide, synthesized to contain no free chlorine, can photolyze to produce hypochlorite ion. At acid pH, this reaction will produce $HOCl$, which can undergo chlorination reactions.

Zika et al. (*3*) also showed that the major stable end products of photolysis of ClO_2 in aqueous solution are Cl^-, chlorate ion (ClO_3^-), and oxygen. The first two species are produced through hydrolysis of chlorous acid anhydride (Cl_2O_3) and the dimeric form of chlorine monoxide (Cl_2O_2), with ClO^- and $Cl^{\cdot}$. Free radicals also are involved in the reaction sequences.

When chlorine dioxide undergoes reaction as a chemical oxidant, it is reduced to chlorite ion. If other strong oxidizing agents are present in solution (ozone and/or free residual chlorine, for example) chlorite can be reoxidized back to ClO_2. However, ozone will continue to oxidize chlorite (or ClO_2) to chlorate ion (ClO_3^-). Thus when both ozone and chlorite/ClO_2 are present initially in aqueous solution, Fiessinger et al. (*4*) consider ClO_2 to be merely an intermediate reaction product between chlorite and chlorate ions.

In conducting studies at operating French water treatment plants, Fiessinger et al. (*4*) showed that granular activated carbon (GAC) decomposes chlorite ion but not chlorate ion. Thus, when both ClO_2 and ozone are used in drinking water treatment processes, these researchers recommend either that ozone should be used and its residual allowed to decay before addition of ClO_2, or that ClO_2 treatment should be followed by GAC treatment (to decompose chlorite ion) before ozonation.

Monochloramine. Monochloramine can be generated by adding chlorine to a solution containing ammonia, by adding ammonia to a solution containing free residual chlorine, or by premixing pure solutions of ammonia and chlorine, then adding the preformed chloramine solution to the water to be treated.

Addition of ammonia to a chlorine solution has the disadvantage of first developing a free chlorine residual, which will produce many chlorinated and/or oxidation products initially. Addition of chlorine to an ammonia

Table 3. Major by-products of primary oxidants/disinfectants.

Oxidant/disinfectant	Major by-products
Chlorine	$HOCl$, $(OCl)^-$, Cl^-
Chlorine dioxide	$(ClO_2)^-$, $(ClO_3)^-$, Cl^-, + chlorine (if prepared using excess chlorine)
Monochloramine	Excess chlorine or ammonia, depending on method of preparation; hydrolysis to $HOCl/(OCl)^-$
Ozone	Oxygen, $(OH)\cdot$

solution minimizes development of free residual chlorine, except at the specific point of addition of chlorine. The third overcomes the disadvantages of the first two methods.

On the other hand, monochloramine hydrolyzes slowly in aqueous solution, producing hypochlorite (at alkaline pH) or hypochlorous acid (at acid pH). This hydrolysis occurs faster at lower pH levels (*5*). Thus the opportunity for chlorination reactions occurring through hypochlorous acid/hypochlorite always is present, even with preformed monochloramine solutions.

Ozone. Ozone (O_3) reacts by two different mechanisms in aqueous solution. At low pH (below 6), ozone reacts directly as the ozone molecule. At high pH (above 8), ozone dissociates into hydroxyl free radicals [$(OH)^{\cdot}$], which are the oxidizing species. Between pH 6 and 8, ozone reacts by either or both pathways, with hydroxyl free radicals predominating as the pH approaches 8.

Combining ozone with ultraviolet radiation or with hydrogen peroxide accelerates the production of hydroxyl free radicals from ozone. Hydroxyl free radicals also are generated from hydrogen peroxide (H_2O_2), which is produced during many ozone oxidations of organic materials, or which can be added during or prior to ozonation.

The presence of free radical scavengers, particularly bicarbonate ion, decreases the accelerating effects of hydroxyl free radicals on oxidation reactions. The major by-product of the reduction of ozone is oxygen.

Summary. Table 3 shows the major by-products formed during the reduction of the four primary oxidants/disinfectants.

Reactions of Oxidants with Inorganic Substrates

Chlorine. Bromide ion, nitrite ion, ammonia, sulfide, iron(II), and manganese(II) are components frequently encountered in drinking water supplies. Each of these materials is reactive with free chlorine (hypochlorous acid). The divalent metallic ions and sulfide ion are oxidized to their higher valence states. Nitrite ion forms nitrate ion, and bromide ion is oxidized to free bromine. In turn, free bromine hydrolyzes to produce hypobromous acid and hypobromite ion.

Ammonia reacts with free chlorine to produce monochloramine, dichloramine, and nitrogen trichloride, depending on the stoichiometries of the reactants as well

as on the solution pH. Under proper conditions, monochloramine may be the only product formed. If sufficient excess chlorine is present, all ammonia-nitrogen can be converted to elemental nitrogen (the breakpoint chlorination process).

Chlorine Dioxide. Unlike chlorine, there is no more than slight reaction of pure chlorine dioxide with ammonia or water. Additionally, the reaction of bromide ion with chlorine dioxide is thermodynamically unfavorable, and does not occur (6).

Aqueous solutions containing 1.5×10^{-4} M ClO_2 and exposed to sunlight produced chloride and chlorate ions as the major ionic products. However, when the solution also contained 1×10^{-4} M bromide ion, bromate ion (BrO_3^-), was observed as an additional product. Although the ClO_2 was photolyzed during the first few minutes, the concentration of BrO_3^- increased only gradually on continued exposure to sunlight.

The Br^- concentration first decreased to 50% of that added initially, and then increased as the reaction proceeded. This finding was interpreted as showing an initially rapid oxidation of Br^- to OBr^-, which then reacted photochemically to produce BrO_3^- and Br^-.

Monochloramine. Bromide ion reacts slowly with monochloramine (NH_2Cl), producing bromochloramine ($NHBrCl$), not hypobromite ion (6). Hypobromite ion reacts rapidly with NH_2Cl, probably producing $NHBrCl$ (7).

Nitrite ion catalyzes the reaction between chloramine and bromide ion, but is not itself oxidized by NH_2Cl (8).

Ozone. As a general rule of thumb, any oxidizable inorganic material will be oxidized when treated with ozone. Bromide ion is oxidized with ozone rapidly to produce hypobromous acid/hypobromite[HOBr/(OBr)]. Hypobromite ion decomposes back to bromide ion. Therefore, bromide ion can act as a catalyst in the destruction of ozone. Excess ozone oxidizes hypobromite ion to bromate ion, the reaction proceeding faster with increasing pH. In the presence of ammonia, bromide is oxidized by ozone to hypobromite which, in turn, reacts with ammonia to produce bromamine.

Nitrite ion reacts almost instantaneously with ozone, forming nitrate ion.

Ozone reacts slowly with hypochlorite ion, producing 77% chloride ion and 23% chlorate ion. The rate of reaction decreases with decreasing pH (as the more stable-to-ozonation HOCl is formed from hypochlorite ion). Therefore, applying ozone to drinking water containing free hypochlorite ion destroys both, decreasing the efficiency of both reagents (9).

Because of the low yield of chlorate ion produced during ozone oxidation of hypochlorite ion, significant quantities are not expected to form in drinking water treatment plants. To ensure the total absence of chlorate ion, however, ozonation should be conducted in the absence of free residual chlorine.

Ozone reacts with chloramine, producing chloride and nitrate ions. The reaction is independent of pH and is about 20% as fast as the reaction of ozone with hypoch-

Table 4. Inorganic oxidation/halogenation products obtained from the four primary oxidant/disinfectants.

Inorganic constituent	Oxidation/halogenation product	Oxidant
Ammonia	Chloramines	Chlorine
Nitrite ion	Nitrate ion	Chlorine, ozone
Bromide ion	Hypobromite ion	ClO_2,[a] ozone, Cl_2
	Hypobromite + bromate	ClO_2,[a] ozone
	BrNHCl	$ClNH_2$
Hypochlorite ion	Chlorate ion (23%) + chloride ion (77%)	Ozone
$ClNH_2$	Chloride + nitrate ions	Ozone
Fe^{+2}; Mn^{+2}	Fe^{+3}; Mn^{+4}	Cl_2, ClO_2, ozone
Mn^{+4}	MnO_4^- (permanganate)	Ozone

[a] In intense sunlight.

lorite ion. Chlorate ion is not produced in this reaction (9).

Ozone oxidizes bromamine to nitrate and bromide ions (9).

Ozone does not oxidize chloride ion to chlorine, hypochlorite, or chlorate at any meaningful rate under drinking water treatment plant ozonation conditions (9).

Ozone oxidizes chlorite ion to chlorine dioxide; in turn chlorine dioxide is oxidized by ozone to chlorate ion. Therefore, drinking water ozonation should be conducted in the absence of these two chlorine species (chlorite ion and chlorine dioxide) (9).

Ferrous iron is oxidized rapidly to ferric ions, which hydrolyze, producing the insoluble ferric hydroxide. Manganous ion is oxidized quickly to manganic ion, which hydrolyzes and precipitates as manganese dioxide. Continued ozonation resolubilizes manganese in the form of permanganate ion.

Cyanide ion is rapidly oxidized to cyanate by ozone, which slowly hydrolyzes to nitrogen and CO_2. Ozone oxidizes sulfide ion to free sulfur, then to sulfite ion, and ultimately to sulfate ion.

Summary. Chlorine can react with ammonia to produce monochloramine, dichloramine, and nitrogen trichloride. Bromide ion is oxidized to hypobromite. Nitrite ion is oxidized to nitrate, and ferrous and manganous ions are oxidzed to the ferric and manganic forms, respectively.

Chlorine dioxide does not react with water or ammonia, but does oxidize bromide ion to hypobromite and bromate, but only in intense sunlight and with high concentrations of ClO_2.

Chloramine reacts with bromide ion to produce BrNHCl, not hypobromite. Nitrite ion is not oxidized to nitrate by monochloramine. Ozone oxidizes nearly any oxidizable constituent, except ammonia at drinking water pH ranges. Bromide ion is oxidized to hypobromite, then to bromate ion. Hypochlorite ion is oxidized to chloride ion (77%) and 23% chlorate ion. Chloramine is oxidized to chloride and nitrate ions.

Table 4 summarizes the inorganic oxidation/halogenation products that have been obtained from the four oxidants/disinfectants.

Reactions of Oxidants/Disinfectants with Organic Aliphatic Substances

Chlorine. Acyl compounds and 1,3-diketones (and 1,3-dihydroxyaromatic materials) readily undergo the haloform reaction during aqueous chlorination, producing trihalomethanes (THMs) and nonchlorinated acids (*10*). However, THMs also are produced from other precursors (humic and fulvic acids, for example) and by reaction mechanisms, not yet clearly defined, other than the haloform reaction.

Aldehydic groups in unsaturated compounds can be oxidized to acid groups during aqueous chlorination, without incorporating chlorine into the molecule (*11–13*).

In simulating the migration of vinyl chloride monomer (VCM) from PVC pipes into water, Ando and Sayato (*14*) showed that injection of 10 mg/L quantities of VCM into deionized water, followed by various concentrations of sodium hypochlorite, converted the vinyl chloride into chloroacetaldehyde and chloroacetic acid:

$$H_2C = CHCl + HOCl \rightarrow ClCH_2CHO + ClCH_2COOH$$
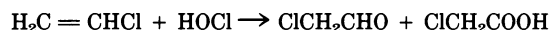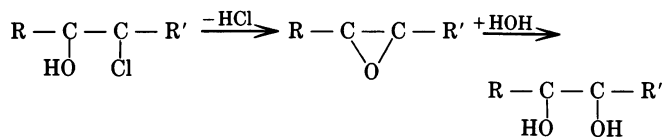
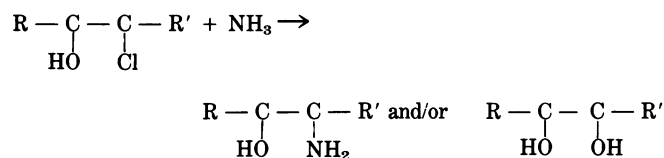It may be significant that additional chlorination did not appear to take place.

During aqueous chlorination, other unsaturated aliphatic compounds appear to add the elements of HOCl (HO and Cl) across the double bond to form chlorohydrins (*15,16*):

$$R - C = C - R' + HOCl \rightarrow R - \underset{\underset{HO}{|}}{C} - \underset{\underset{Cl}{|}}{C} - R'$$
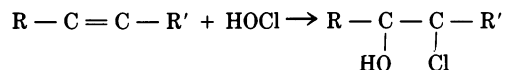
These compounds then can react further (*15*) (1) by dehydrochlorination, i.e., a chlorohydrin can form an epoxide, which itself may further react with water to produce a glycol):

$$R - \underset{\underset{HO}{|}}{C} - \underset{\underset{Cl}{|}}{C} - R' \xrightarrow{-HCl} R - \underset{O}{C - C} - R' \xrightarrow{+HOH}$$

$$R - \underset{\underset{HO}{|}}{C} - \underset{\underset{OH}{|}}{C} - R'$$

(2) by ammoniation; i.e., as in the presence of ammonia, a chlorohydrin can form aminoalcohols and/or glycols:

$$R - \underset{\underset{HO}{|}}{C} - \underset{\underset{Cl}{|}}{C} - R' + NH_3 \rightarrow$$

$$R - \underset{\underset{HO}{|}}{C} - \underset{\underset{NH_2}{|}}{C} - R' \text{ and/or} \quad R - \underset{\underset{HO}{|}}{C} - \underset{\underset{OH}{|}}{C} - R'$$
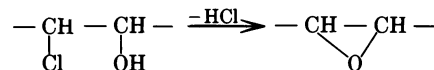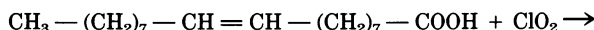
Carlson and Caple (*16*) studied the aqueous chlorination of the mono-unsaturated oleic acid over a wide range of pH values (1.8 to 11.2) and chlorine concentrations (0.51 to 10.2 mg/L) and in the presence of ammonia. They identified a number of the expected products of addition across the double bond, along with a low yield of the 9,10-epoxystearic acid:

$$CH_3(CH_2)_7\underset{O}{\overset{}{CH - CH}}(CH_2)_7COOH$$
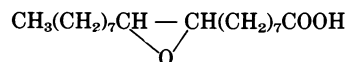
Aliphatic amines react with aqueous chlorine to produce *N*-chloroorganic compounds (*N*-chloroamines). Under virtually all conditions of temperature and pH encountered in drinking water treatment plants, 99% of the free available chlorine was found to react within 0.5 second with a variety of commonly present amines and amino acids to form *N*-chloroamines and *N*-chloroamino acids (*17*). *N*-Chloroorganic compounds are even less bactericidal than monochloramine. Thus the presence of organonitrogen compounds reduces the effectiveness of chlorine as a disinfectant.
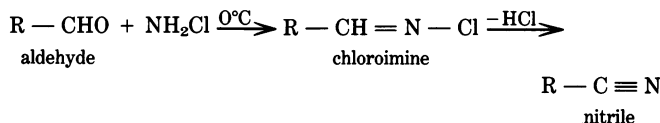
Chlorine Dioxide. ClO$_2$ generally produces more oxidation and less chlorination of organic materials than does HOCl. Saturated aliphatic hydrocarbons are neither oxidized nor chlorinated by ClO$_2$. Aliphatic alcohols can be oxidized with ClO$_2$ to aliphatic acids, which generally are stable to further oxidation by ClO$_2$.

Unsaturated aliphatic acids (e.g., oleic acid) produce a variety of compounds during treatment with ClO$_2$. These compounds include ketones alpha to the point of unsaturation; chloroketones at the originally unsaturated carbon atoms; chlorohydrins; dichloro addition products; and the epoxide. This last type of compound probably is formed by addition of HOCl across the double bond, forming the chlorohydrin, which then dehydrochlorinates to form the epoxide. Formation of this epoxide from oleic acid treated with ClO$_2$ has been observed by two teams of investigators (*18,19*).

$$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - COOH + ClO_2 \rightarrow$$

$$- \underset{\underset{Cl}{|}}{CH} - \underset{\underset{OH}{|}}{CH} - \xrightarrow{-HCl} - \underset{O}{CH - CH} -$$
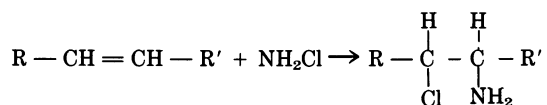
Primary aliphatic amines are essentially unreactive with ClO$_2$. Secondary aliphatic amines react very slowly. Tertiary aliphatic amines react rapidly to produce aldehydes and secondary aliphatic amines, without forming *N*-oxides. However, amines which cannot give up an α-hydrogen atom during oxidation (such as in quinuclidine) do produce *N*-oxides during treatment with ClO$_2$.

Chloramine. Aldehydes and ketones produce amides or chloroimines when treated with monochloramine (*20,21*). Chloroimines derived from aldehydes can produce nitriles, probably by undergoing dehydrohalogenation (*21*).

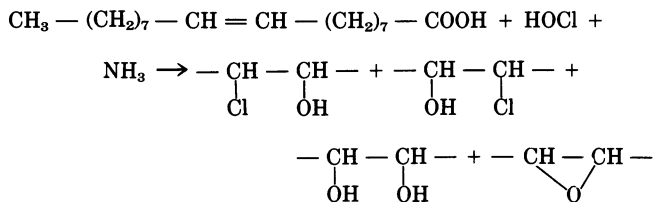$$R - CHO + NH_2Cl \xrightarrow{0°C} R - CH = N - Cl \xrightarrow{-HCl}$$
$$\underset{\text{aldehyde}}{} \qquad \qquad \underset{\text{chloroimine}}{}$$

$$R - C \equiv N$$
$$\underset{\text{nitrile}}{}$$

Some olefins react with NH$_2$Cl by adding the $-$Cl and

—NH$_2$ moieties across the double bond, producing chloroamines (22).

$$R — CH = CH — R' + NH_2Cl \rightarrow R — \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}} - R'$$

Oleic acid plus chlorine in the presence of ammonia produces the same two 9,10-chlorohydrins isolated from chlorine alone; however, the 9,10-glycol and the 9,10-epoxystearic acid also are obtained (16).

$$CH_3 — (CH_2)_7 — CH = CH — (CH_2)_7 — COOH + HOCl +$$

$$NH_3 \rightarrow — \underset{\underset{Cl}{|}}{CH} — \underset{\underset{OH}{|}}{CH} — + — \underset{\underset{OH}{|}}{CH} — \underset{\underset{Cl}{|}}{CH} — +$$

$$— \underset{\underset{OH}{|}}{CH} — \underset{\underset{OH}{|}}{CH} — + — \underset{\diagdown O \diagup}{CH — CH} —$$

Chlorine transfer from the monochloramine-nitrogen atom to the nitrogen atom of amines, amino acids, and peptides, occurs readily in aqueous solution over the pH range 2–10. This transfer occurs both indirectly by hydrolysis of NH$_2$Cl to produce HOCl, as well as by a direct reaction of NH$_2$Cl. Reaction products are organic N-chloro derivatives, or organochloroamines (17).

Ozone. Ozone oxidations of aliphatic compounds proceed through organic ozonides, peroxides, diperoxides, triperoxides, hydroalkyl peroxides, and peroxyacids. These types of intermediates are readily isolated in nonaqueous solvents. In aqueous solvents, however, these intermediates are unstable, decomposing rapidly to form simpler products (aldehydes, ketones, carboxylic acids, and H$_2$O$_2$).

Although ozone is capable of oxidizing many organic compounds completely to CO$_2$ and water, this conversion normally requires large doses of ozone (> 3 moles O$_3$/mole of organic compound) and long reaction times (sometimes hours). Under drinking water treatment plant ozonation conditions (1 to 5 mg/L applied ozone dosage; 5 to 20 minutes contact time), organic compounds more often are only partially oxidized. The oxidized organic materials usually are more polar, of lower molecular weight, more biodegradable, and more readily removed from solution by chemical treatment and filtration.

Oxalic acid (HOOC–COOH) is commonly found as a "final" oxidation product of many aliphatic (and aromatic and heterocyclic) organic materials, because of its very slow rate of oxidation with ozone. Acetic acid is another "final" oxidation product which also is resistant to further oxidation with ozone.

Formic acid and formaldehyde also are formed in the later stages of oxidation of many organic materials. However, these two organic compounds are rapidly oxidized to CO$_2$ and water upon continued ozonation.

Ozone oxidation rates of intermediate organic oxidation products usually are slower than the oxidation rates of the original compounds.

In general, ozonation of aliphatic unsaturated compounds results in cleavage of the double bond(s), producing aldehydes, ketones, and/or carboxylic acids. Formation of the latter compounds results in a decrease in pH values. Ozonation of oleic acid has produced small quantities of the same epoxide isloated during chlorination of oleic acid (16).

Hydrocarbons also have been isolated during ozone oxidation of unsaturated aliphatic compounds, although in minor amounts. The longer length of the carbon chains in these hydrocarbon products suggests cleavage of the double bond, followed by formation of a hydrocarbon free radical, then coupling of two hydrocarbon free radicals.

Chlorinated aliphatic compounds are oxidized by ozone more slowly than are the corresponding nonchlorinated materials. Ozonation or UV/ozonation ruptures carbon–chlorine bonds, forming chloride ion and the same aldehydes, ketones, and/or carboxylic acids produced by ozonation of their nonchlorinated analogues.

The following aliphatic compounds have been shown to be unreactive to ozone, under drinking water treatment plant conditions: oxalic acid, acetic acid, glycerol, urea, saturated aliphatic and alicyclic hydrocarbons, pelargonic acid, hexanoic acid, octanoic acid, and the explosive RDX (cyclonite).

Discussion. HOCl adds across the double bond of oleic acid to produce the corresponding chlorohydrins and small amounts of the epoxy derivative. Chlorine dioxide produces the same chlorohydrins, the *vic*-dichloro derivative, and the epoxide. Chloramine forms the chlorhydrins, the *vic*-glycol, and small amounts of the epoxide. Ozone produces small amounts of the epoxide. Chlorine, ozone, and ClO$_2$ produce higher yields of compounds in which the original oleic double bond was ruptured.

Chlorine dioxide with aliphatic compounds generally produces more oxidation products than chlorination products, particularly if it has been generated to be free of residual chlorine.

Amine and amido functions react rapidly with free chlorine (99% in about 0.5 sec), forming N-chloro derivatives, which are even less bactericidal than monochloramine. More importantly, when free ammonia and an organic amine or amide are present, added chlorine reacts preferentially with the organic nitrogen before it reacts with the ammonia to form chloramines.

Chlorine dioxide does not react with primary amines, reacts very slowly with secondary amines, and with tertiary amines ClO$_2$ produces secondary aliphatic amines, without forming N-oxides. With aldehydes and ketones, monochloramine produces chloroimines, which (from aldehydes) decompose to produce nitriles. NH$_2$Cl adds across olefinic double bonds to produce chloroamines. The chlorine atom in monochloramine transfers rapidly to the nitrogen function in amines, amino acids, and peptides, producing N-chloro derivatives. These

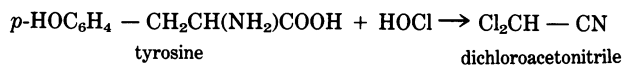react further to produce nitriles (see next section for details).

Ozone generally is not reactive with saturated aliphatic hydrocarbons. However, other types of aliphatic compounds, particularly olefins, are readily oxidized through ozonides, peroxides, and hydroperoxide intermediates to form aldehydes, ketones, and acids. A by-product of all organic oxidations with ozone is hydrogen peroxide. In the presence of more ozone, however, the H_2O_2 is decomposed into hydroxyl free radicals, which are more powerful oxidizing agents than the ozone molecule.

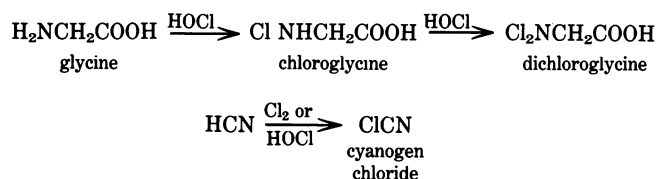## Reactions of Oxidants/Disinfectants with Amino Acids

Amino acids are liberated by microorganisms in natural media and are found in raw water supplies in concentrations of 5 to 2,000 μg/L, either in the free state or combined as peptides, nucleic acids, purines, pyrimidines, and proteins (*23*). Flocculation/decantation does not necessarily remove amino acids during water treatment, and they can be present at the final disinfection stage. These nontoxic materials can be changed structurally upon treatment with oxidizing (disinfection) agents.

Chlorine. Amino acids react with aqueous chlorine to form N-mono- or N,N-dichlorinated derivatives, depending on whether chlorine is added in excess. Subsequent decomposition of these compounds is affected by the nature of the original amine group. If it was a primary amine, the decomposition products are aldehydes, ketones, carbonic acid, chloride ion, and ammonia. If it was a secondary amino group, the same products are formed, except that the corresponding amine replaces the ammonia (*24*).

Trehy and Bieber (*25*) identified dichloroacetonitrile as a product of chlorination of tyrosine in water:

$$p\text{-HOC}_6\text{H}_4 - \text{CH}_2\text{CH(NH}_2)\text{COOH} + \text{HOCl} \rightarrow \text{Cl}_2\text{CH} - \text{CN}$$

<div align="center">tyrosine   dichloroacetonitrile</div>

Sakuri and Sawamura (*26*) found that monochloroglycine, formed in the first stage of the reaction of glycine with hypochlorite, was further chlorinated to give dichloroglycine by the action of excess hypochlorite. The formed dichloroglycine underwent decarboxylation and dehydrochlorination to form HCN, which then was chlorinated by chlorine or by excess hypochlorite to form cyanogen chloride, ClCN. One mole of glycine required three moles of hypochlorite for the formation of the equivalent ClCN.

$$\text{H}_2\text{NCH}_2\text{COOH} \xrightarrow{\text{HOCl}} \text{Cl NHCH}_2\text{COOH} \xrightarrow{\text{HOCl}} \text{Cl}_2\text{NCH}_2\text{COOH}$$

<div align="center">glycine   chloroglycine   dichloroglycine</div>

$$\text{HCN} \xrightarrow{\text{Cl}_2 \text{ or HOCl}} \text{ClCN}$$

<div align="center">cyanogen chloride</div>

Qualls and Johnson (*27*) showed that the rate of chlorination of ammonia was considerably slower than the rate of chlorination of glycylglycine. This peptide outcompeted ammonia for the available HOCl until an excess of HOCl was added beyond that required to form N-chloroglycylglycine.

Le Cloirec et al. (*28*) isolated the following compounds from the chlorination of alanine [$\text{CH}_3\text{CH (NH}_2)\text{COOH}$] using chlorine/amino acid ratios (x) between 0.5 and 6: NH_2Cl (chloramine), $NHCl_2$ + NCl_3 (dichloramine + nitrogen trichloride), CH_3CHO (acetaldehyde), CH_3CN (acetonitrile), $\text{CH}_3\text{CH} = \text{NH}$ (acetimine), and CH_3COOH (traces) (acetic acid). Alanine was totally destroyed when x was equal to or greater than 2. Dichloramine and nitrogen trichloride appeared at $x = 1$ and increased when x was above 2.5. Both acetaldehyde and acetonitrile were present in solution, the concentration of acetaldehyde peaking at almost the original alanine concentration when x approached 1.5. The concentration of acetonitrile increased rapidly as the concentration of acetaldehyde decreased, peaked when $x = 4$, and then decreased only slowly afterward.

These observations indicated that acetaldehyde may be an intermediate in the formation of acetonitrile. To verify this hypothesis, a solution was prepared containing acetaldehyde and the chloramines formed by the action of NaOCl on NH_4^+ under the same conditions. Acetonitrile formed at essentially the same rate as during the chlorination of alanine and at the expense of acetaldehyde.

Chlorine Dioxide. Aliphatic amino acids oxidize slowly in the presence of ClO_2 free of residual chlorine and form nonchlorinated oxidation products. Glycine produced formaldehyde and CO_2. Phenylalanine produced small quantities of benzylic acid, benzoic acid, mandelic acid, and traces of phenylacetaldehyde.

Sulfur-containing amino acids (cystine and methionine) oxidize at the S-atoms to produce bisulfoxide and sulfonic acid derivatives.

Monochloramine. In the presence of amines, amino acids, and/or peptides, chloramine is even less effective as a disinfectant, because of its tendency to form N-organochloramines by chlorine transfer, with concomitant destruction of NH_2Cl. For example, with small amounts of glycine (0.1–0.25 mg/L) present in ammoniated water, the addition of chlorine forms N-chloroglycine preferentially to forming NH_2Cl (*29*).

N,N-Dichloro-α-amino acids decompose rapidly, forming nitriles, CO_2, and chloride ion. This reaction is at least one order of magnitude faster than the corresponding decomposition of N-monochloro-α-amino acids (*30*). This is a second pathway to the production of nitriles in chlorinated waters.

Peptides form N-chloro derivatives with monochloramine only at the terminal $-NH_2$ groups. Amide nitrogen atoms in the body of the peptide chains are unreactive to NH_2Cl (*30*).

Ozone. The amino acid alanine is decomposed readily by ozonation liberating all of the organic nitrogen as both ammonium and nitrate ions (*31*). No acetonitrile is

formed by ozonation of alanine (28). Phenylalanine is less readily decomposed by ozone, and 30% to 75% of the organic nitrogen remains combined in the organic oxidation products (31).

Small amounts (but larger than trace quantities) of polymeric materials (molecular weight 500 to 70,000) are produced during ozonation of phenylalanine, indicating that it is possible to synthesize polymeric materials by ozonation of this type of difunctional monomeric compound (28).

Discussion. When amino acids or proteinaceous materials (peptides) are treated with chlorine, N-monochloro and/or N,N-dichloro derivatives are produced rapidly. Even when ammonia is present, these N-chloroamino derivatives are produced selectively over the formation of monochloramine. Upon further reaction of these chlorinated compounds, nitriles, hydrogen cyanide, and cyanogen chloride have been identified, particularly when the molar ratio of chlorine to amino acid (alanine) is as high as 4.

The decomposition rate of N,N-dichloro-α-amino acids is at least one order of magnitude faster than that of the corresponding N-monochloro-α-amino acid.

It has been proven that acetaldehyde produces acetonitrile in the presence of the intermediate chlorinated amino acids. This leads to speculation that other aldehydes may also be nitrile precursors in the presence of chlorinated amino acids. More studies are required to confirm this hypothesis.

It thus would appear that to minimize the formation of nitriles, HCN, and cyanogen compounds, the formation of N,N-dichloroamino acids should be avoided, or at least minimized. This can be accomplished either by removing the amino acids before chlorine is added, or by avoiding the addition of large quantities of chlorine (i.e., breakpoint chlorination). Since amino acids are ubiquitous in raw water supplies, treatment conditions should be developed for their removal, or at least for rupturing the carbon–nitrogen bond to eliminate the organic amine functional group, before addition of chlorine.

Neither chlorine dioxide nor ozone produces N-chlorinated derivatives of amino acids. In fact, both oxidants decompose many amino acids and peptides, although ClO_2 appears to be unreactive with many amino acids. With alanine, for example, ClO_2 is unreactive, but ozone converts all the organic nitrogen to ammonium and nitrate ions. This would suggest that preozonation of raw water supplies could be used to destroy amino acids, prior to chlorination or chloramination.

However, phenylalanine is not as easily oxidized, even with ozone; some 30 to 75% of the organic nitrogen remains bound in the organic oxidation products. As before, more studies should be conducted to confirm these potentials.

Reactions of Oxidants/Disinfectants with Organic Aromatic and Cyclic Compounds

The three strong oxidants (chlorine, chlorine dioxide, ozone) act similarly as chemical oxidizing agents with respect to phenols, aromatic amines and amino acids, and pesticides. That is, aromatic rings are hydroxylated in a first step, then quinones are produced as initial reaction intermediates. With higher dosages and/or longer reaction times, ring rupture generally occurs, leading to the formation of aliphatic mono- and di-acids.

Chlorine also produces chlorinated aromatic materials, which lead to chlorinated aliphatic compounds upon ring rupture. Yields of ring-chlorinated products are higher at low molar ratios of chlorine to phenol. At higher ratios, ring-ruptured products predominate.

Pure chlorine dioxide behaves more like chlorine than ozone with respect to phenol, in that similar products are obtained as with the use of HOCl. This statement applies, however, only if the concentration of phenol is in stoichiometric excess over that of the ClO_2. When chlorine dioxide is present in excess, p-benzoquinone and aromatic carboxylic acids are produced (32). On the other hand, aromatic amino acids undergo oxidation reactions, rather than chlorination, with pure ClO_2.

Chlorine produces small yields of nonchlorinated epoxy derivatives from abietic acid and cholesterol. Ozone also produces the same epoxy compounds from cholesterol and abietic acid (15,16), and from acenaphthylene as well (33).

Ozone (34) and chlorine dioxide (35) have been shown to oxidize the pesticides Parathion and Malathion initially to the more toxic intermediates, paraoxon and malaoxon, respectively. Continued ozonation has been shown to destroy these intermediates, producing simpler decomposition products. Hoffmann and Eichelsdörfer (36) showed that ozonation of heptachlor produced a quantitative yield of heptachlor epoxide, which itself is stable to further decomposition by ozone.

A number of pesticides are resistant to chemical oxidation, even by ozone. If these pesticides are present in water supplies, procedures other than chemical oxidation must be used for their removal.

Ozonation of phenol can produce resorcinol, which is a know THM precursor. The initial rate of oxidation of phenolic materials with ozone is very fast, reflecting the ease of oxidation of these materials. During continued ozonation, however, their rates of oxidation slow considerably, reflecting the slower oxidizability of their oxidation products.

Ozonation of chlorinated aromatic compounds ruptures the carbon–chlorine bonds, producing chloride ions and ring-ruptured, aliphatic products. Aniline produces the same oxidation products as phenol during ozonation, plus nitrate ions and ammonia (37,38).

Some oxidative coupling of phenolic materials has been observed as a result of ozonation, producing higher molecular weight materials (39). This behavior might partially explain the ability of ozone to microflocculate soluble impurities in water supplies.

The ratio of the concentration of 5-day biochemical oxygen demand to total organic carbon concentration (BOD_5/TOC) increases upon ozonation and increases faster after ring rupture has occurred (37). This shows that some biorefractory compounds can be partially ox-

idized during ozonation to produce organic materials which are more easily biodegradable.

Polycyclic aromatic compounds and some pesticides (40) have been shown to be readily adsorbed by humic materials and soil particles, which provide a shielding effect toward ozonation.

Monochloramine in the presence of excess ammonia reacts with some aromatic hydrocarbons (benzene, toluene, o-, m-, and p-xylene, and naphthalene) to produce cyanogen chloride (41,42). With phenol, p-aminophenol is produced initially, and chlorophenols are identified after the solution has stood for several days (43–45). Aromatic acids, which are normally THM precursors, do not produce THMs with chloramine, but rather form the corresponding chlorophenolic aromatic acids (46).

Reactions of Oxidants/Disinfectants with Heterocyclic Compounds

Amino acids, nucleic acid bases, purines, and pyrimidines have been identified in surface water supplies, particularly when algae levels in the raw water supplies are high (23). Purines and pyrimidines also are components of nucleic acids in bacteria and are known to produce mutagens upon chlorination. These materials may be precursors for nitriles and chloroform (47).

Chlorine. 5-Chlorouracil and 5-chlorocytosine were identified in the acid hydrolysates of the nucleic acids separated from bacteria after parts-per-million (ppm) chlorine disinfection of water supplies (48). Patton et al. (49) and Gould et al. (50,51) confirmed that cytosine and uracil react with HOCl in aqueous solution to produce the 5-chloro derivatives. 5-Chlorouracil has been shown to be mutagenic.

Franssen and van der Plas (52) isolated 5-monochloro- and 5,5-dichlorobarbituric acids from the chlorination of barbituric acid and its derivatives.

Chlorine Dioxide. Nitrogen heterocycles generally produce oxidation products rather than chlorination products upon treatment with ClO_2.

Chloramine. Lin and Carlson (53) studied the reaction of a number of environmentally significant heterocycles with aqueous chlorine, chlorine dioxide and chloramine. Chloramine generally was quite unreactive with these heterocycles, except at low pH, where hydrolysis to form a significant amount of HOCl occurred, yielding increased amounts of chlorinated products. In general, chloramine required much longer reaction times to produce > 95% reaction than did hypochlorite or ClO_2 at pH 7.0.

Summary. Chlorination of uracil and cytosine produces the mutagenic 5-chloro derivatives. Chlorine dioxide generally produces oxidation products rather than chlorinated derivatives. Chloramine reacts very slowly, if at all, with heterocyclic materials, except at low pH ranges (~3), where hydrolysis to HOCl occurs, allowing chlorination to occur. Ozone produces a variety of nonchlorinated heterocyclic oxidation products.

Reactions of Oxidants/Disinfectants with Humic and Other Natural Materials

Chlorine. From the aqueous chlorination of various aquatic humic materials, Stevens et al. (54) identified 98 specific organic compounds, including 47 discrete compounds containing chlorine and 51 discrete compounds that did not contain chlorine. De Leer et al. (55) identified over 100 different reaction products from the chlorination of soil humic acid material.

Christman et al. (56) showed that the products of exhaustive chlorination of aquatic humic materials generally fall into three broad structural categories: nonchlorinated substituted aromatics, chlorinated straight-chain acids, and nonchlorinated straight-chain aliphatic acids. From the aqueous chlorination of humic materials, nonvolatile halogen-containing materials account for about 43% of the total organic halogen found. Chloroform represents about 95% of the volatile organics formed. The nonvolatile halogenated fraction is produced in higher yield under acidic conditions compared to that produced under alkaline conditions.

Seeger et al. (57) showed that at low chlorine dosages, which are more typical of those conditions found in drinking water treatment plants and their distribution systems, a large number of ring-chlorinated aromatic acids is obtained, in addition to the numerous nonchlorinated aromatic and aliphatic compounds identified by earlier investigators.

Chlorinated fulvic acid samples contain about 60% more organic-bound chlorine than do chlorinated humic acid samples, even when the humic chlorination is conducted over twice the reaction time (58).

The principal chlorinated products formed during aqueous chlorination of fulvic acids at pH 7 are: trichloroacetic acid, 69%; dichloroacetic acid, 9.5%; chloroform, 19%; and dichlorosuccinic acid, 4.5%. These compounds represent 53% of the total organic halogen content, and about 14% of the starting organic materials (about 4% of the original TOC). Note that the amount of trichloroacetic acid is more than triple that of chloroform (59).

Cyano-substituted compounds (nitriles) recently have been identified as products of aqueous chlorination of humic/fulvic materials (54,55,60). These compounds include: chloroacetonitrile, dichloroacetonitrile, trichloroacetonitrile, dichloropropanenitrile, dichloropropenenitrile, trichloropropenenitrile, 3-cyanobutanoic acid, and 4-cyanobutanoic acid. It is possible that these compounds arise from reactions of chlorine with amino acids or proteinaceous materials to form N,N-dichloroamino acids, followed by dehydrohalogenation to the nitriles.

Chlorinated aliphatic aldehydes also have been identified. These compounds might be precursors of the nitriles, as well as of chlorinated acids, which are logical hydrolysis/oxidation products of the above nitriles. For example, di- and trichloroacetaldehydes, and mono-, di-, and trichloroacetic acids (60) could be formed by hydrolysis of the corresponding nitriles.

Chloropicrin (Cl_3CNO_2) has been identified recently

(61), along with other volatile organic chemicals, during chlorination studies with humic and fulvic materials. Precursors include aminoacids and nitrite ion. Ammonia must be absent. Chloropicrin was formed more rapidly at pH 10 than at pH 7, and the presence of nitrite ion is essential.

Duguet et al. (62) and Mallevialle et al. (63), isolated chloropicrin from drinking water supplies that had been prechlorinated. They also showed that the addition of reducing agents to chlorinated drinking water supplies with the objective of destroying excess free residual chlorine, also converts any chloropicrin present to chloroform:

$$Cl_3 - C - NO_2 + reducing\ agent \rightarrow CHCl_3$$
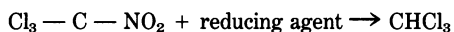
In light of this fact, it is not surprising that chloropicrin has escaped more general detection and reporting in drinking water supplies. If more than the stoichiometric amount of sulfite or thiosulfate required to quench free residual chlorine is added, chloropicrin will be destroyed. Equally significant, however, the amount of chloroform found will be higher than that actually produced as a result of chlorination.

Chloropicrin also has been identified as a product of chlorination of resorcinol. Filtration through GAC was found to destroy chloropicrin (62,63). These authors suggest that the simplest way to control chloropicrin formation in water supplies is by abandoning breakpoint prechlorination.

Chlorine Dioxide. Chlorine dioxide does not produce trihalomethanes with humic materials, except when free chlorine is present. From pure chlorine dioxide, the following four general classes of oxidation products were obtained at pH 3 and 7.8 (64): benzenepolycarboxylic acids, aliphatic dibasic acids (greater yields from ClO_2 than from Cl_2 or $KMnO_4$), carboxyphenylglyoxylic acids, and aliphatic monobasic acids. Compounds identified in these studies were similar to those identified during experiments using chlorine, ozone, and potassium permanganate as the oxidants.

Several derivatives of furan and dioxane also were identified, as well as several chlorinated compounds. Far fewer chlorinated products are formed by reaction with ClO_2 than with Cl_2. An average of 30% of the original TOC was removed by treatment with ClO_2.

Monochloramine. Chloramination of humic and fulvic materials produced no identifiable chlorination or oxidation products in diethyl ether extracts, although the fulvic materials tested exerted a demand for 0.13 mole NH_2Cl mole of carbon after 24 hr at pH 9, and the color of the fulvic material had been bleached. This behavior might be explained by selective addition reactions of NH_2Cl across olefinic sites in the fulvic molecules, thus destroying some or all of the chromophoric moieties (57).

Ozone. Ozonation of natural humic and fulvic acids released the pesticides Lindane and DDT, along with iron and manganese cations. With small quantities of ozone simulating dosages used in drinking water treatment plants (0.1 to 2 mg/L), humic acids depolymerized

and, in the majority of experiments, turbidities increased, and BOD_5 increased (65).

Ozonation of humic and fulvic materials cleaves the polymeric chains (> 1000) and forms lower molecular weight fragments (< 1000) and aliphatic acids and ketones, phenols, and phthalic acids (66,67).

Higher molecular weight polymeric humic materials (> 300,000) are decomposed during ozonation into shorter fragments (< 5,000). In addition, the ozonized solutions now contain higher concentrations of phenolic constituents than are present before ozonation. These phenolic compounds might be liberated by decomposition of iron and manganese complexes (68).

More recent studies have shown that aromatic acids are virtually eliminated after one hour of ozonation, which conditions provide much higher dosages of ozone than normally encountered during drinking water ozonation. In some cases, tetrachloro-, and pentachloro-, and hexachlorobenzenes have been isolated from solutions of humic materials ozonized for 1 hr. These chlorinated compounds probably were present as soil humic contaminants and were released as the humic material decomposed during ozonation (69).

Oxidation of fulvic acids caused depolymerization, and several fractions of lower molecular weight materials were isolated. Ozonation produced more low molecular weight compounds from fulvic acids than did $KMnO_4$ oxidation. Ozone/UV produced fewer low molecular weight compounds than ozonation alone, probably caused by more complete oxidation of the carbon to CO_2 (70). GAC adsorption rates of ozonized humic acids decrease to a minimum at a range of consumed ozone of 0.13–0.3 mg O_3/mg organic C, then increase with increased ozone dosage. At 1.08 mg O_3/mg C, the biodegradability of the ozonized solutions quadrupled (71). Because ozonation increases biodegradability of humic and fulvic materials, removal of dissolved organic carbon can be improved further by following ozone oxidation with a biological treatment before chlorination (72).

Four major classes of compounds have been isolated from ozonized solutions of humic and fulvic acids (57,72): benzenecarboxylic acids, aliphatic dibasic acids (C_4 to C_{10}), aliphatic monobasic acids (C_2 and higher), and carboxyphenylglyoxylic acids. The nonchlorinated, aromatic, and aliphatic compounds identified are identical or very similar to those obtained when treating the same humic or fulvic materials with chlorine, chlorine dioxide, or potassium permanganate.

Discussion. From the complete chlorination of humic and fulvic acids, more than 100 discrete compounds have been identified. About half of these are nonchlorinated, and both classes consist of substituted aromatic compounds and straight-chain aliphatic mono-, di-, and polycarboxylic acids. About half the total halogen-containing material is nonvolatile, and chloroform comprises about 95% of the volatile organics produced.

Chlorinated products obtained in highest yield include trichloroacetic acid (69%), chloroform (19%), dichlo-

roacetic acid (9.5%), and dichlorosuccinic acid (4.5%). When chlorination conditions that are closer to those used in drinking water treatment plants (maximum 20 mg/L chlorine doses) are used, more ring-chlorinated aromatic compounds can be isolated.

Many nitriles have been isolated from chlorination of humic/fulvic materials, along with chlorinated aldehydes and chlorinated acids. As discussed in the preceding section dealing with amino acids, aldehydes in the presence of ammonia and chlorine can be precursors of nitriles. Furthermore, hydrolysis of chlorinated acetonitriles (which have been identified from the chlorination of humic materials) would be expected to produce the corresponding chloroacetic acids.

Chlorination of α-terpineol produces a variety of chlorinated derivatives, plus a nonchlorinated epoxide. At pH 10, the yield of epoxide is 39%, which decreases to 1–3% yield at pH 3.

Oxidation of humic and fulvic materials with chlorine dioxide, ozone, and alkaline permanganate forms nonchlorinated oxidation products, which are similar to those produced during chlorination. The major classes obtained from ozonation are benzenecarboxylic acids, C_4–C_{10} aliphatic dibasic acids, C_2 and higher aliphatic monobasic acids, and carboxyphenylglyoxylic acids.

Ozone oxidation of humic/fulvic materials generally lowers the molecular weights, and sometimes liberates entrapped or complexed pesticides (Lindane and DDT) and heavy metals (iron and manganese). At the same time, turbidities and BOD_5 increases. In some cases, the BOD_5 quadruples. Adsorbability of the ozonized organics can decrease at low levels of ozonation (0.13–0.3 mg ozone consumed/mg organic carbon), but then increases with increasing ozone dosage.

Monochloramine produces no products as yet identified, although humics and fulvics exert strong oxidant demands. Higher nonpurgeable total organic halogen concentrations were found (9%–40% higher) with chloramine treatment of fulvic materials than with chlorine. These materials had higher molecular weights and were less polar than the same materials produced by chlorination.

Conclusions

At our current state of knowledge with regard to the chemistries of specific organic materials known to be contained in raw water supplies with respect to the oxidants/disinfectants currently available and used in water treatment, no current water treatment process appears to be able to guarantee the total absence of oxidation products.

Reactions of free chlorine and monochloramine with organonitrogen moieties in amino acids, amines, and peptides can produce nitriles by formation of N,N-dichloro derivatives, followed by decomposition. Aldehydes in the presence of ammonia and chlorine also have been shown to produce nitriles through the same mechanism.

In the presence of nitrite ion, amino acids and chlorine

produce chloropicrin (nitrotrichloromethane). Addition of strong reducing agents converts this material to chloroform. Thus it is possible that many early analyses for trihalomethanes have not found chloropicrin because of the prompt addition of thiosulfate to destroy free residual chlorine. If this has occurred, these analyses for the amount of chloroform produced during chlorination may have been overstated by the amount of chloropicrin converted to chloroform.

Since the concentration of amino acids and peptides is highest in raw drinking water, the preceding conclusions lead to consideration of the recommendation that breakpoint chlorination of raw waters should be abandoned in favor of other procedures that will remove these nitrogen-containing materials before chlorine is added.

To minimize the formation of chlorinated organic materials, as much organic material as possible should be removed before chlorine is added to the water.

Chlorine dioxide generally produces fewer chlorination products than does free chlorine. Amines, amino acids, and peptide nitrogen groups do not form N-chloro derivatives with ClO_2.

Preoxidation of water supplies with ozone or chlorine dioxide before chlorination produces aldehydes, ketones, and acids. Unless the aldehydes are removed (by flocculation, adsorption, or further oxidation) before treatment with ammonia and chlorine, nitriles could be produced.

Epoxide compounds have been identified in laboratory studies of aqueous solutions of oleic acid, abietic acid, cholesterol, α-terpineol, and acenaphthylene. The same nonchlorinated epoxy derivative of oleic acid was produced by treatment with chlorine, ozone, chlorine dioxide, and chloramine. Abietic acid and cholesterol formed the same epoxy derivatives from chlorine and from ozone (no experiments were conducted with ClO_2). Chlorination of α-terpineol produced a nonchlorinated epoxy compound in addition to chlorinated products. Ozonation of acenaphthylene produced the corresponding epoxy derivative, in addition to the more normal oxidation products. Ozonation of heptachlor quantitatively produces heptachlor epoxide which is stable to further ozonation.

Chlorine dioxide in strong sunlight, and aqueous chlorine (HOCl) oxidize bromide ion to hypobromite ion. Ozone also will oxidize bromide ion to hypobromite ion, and additionally will oxidize bromide/hypobromite ions to bromate ion. Thus, waters containing bromide ion will have the potential for producing not only brominated trihalomethanes, but other brominated organic materials.

Ozone reacts with hypochlorite ions, producing chloride and chlorate ions; with chlorine dioxide to produce chlorate ion; with chlorite ion to produce ClO_2 and chlorate ion; and with monochloramine to produce chloride and nitrate ions. Therefore, ozonation processes should be conducted in the absence of these inorganic materials. Any residual ozone should be destroyed before

any of these halogenated materials are added for disinfection.

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